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MODIFICATION OF CARBON BLACK

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Abstract

PURPOSE: To improve the thermal stability of carbon black in acid treatment, without changing the volume resistivity, by heating carbon black in an inert gas atmosphere at a specific temperature in the presence of a higher fatty acid.

CONSTITUTION: Carbon black is modified by heating at 250-800 deg.C, preferably 350-400 deg.C in an inert gas atmosphere such as N₂ in the presence of a higher fatty acid (preferably a 10-20C fatty acid such as lauric acid, stearic acid, oleic acid, etc.) for 1-10hr. It is preferable to treat the carbon black with a mineral acid such as hydrochloric acid, sulfuric acid, etc. (preferably at 1-10% concentration for 1-10hr) prior to the heat-treatment.

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METHOD FOR THE MODIFICATION OF CARBON BLACK

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[The amendments have been incorporated into the text of the translation.]

Claims

1. A method for the modification of carbon black characterized by the fact that carbon black is subjected to a heating treatment at a temperature of 250-800°C under an inert gas atmosphere in the presence of a higher fatty acid.
2. The method described in Claim 1 in which carbon black is treated with a mineral acid prior to said treatment.

Detailed explanation of the invention

The present invention relates to a method for improving the quality of carbon black (also called CB hereafter).

Recently, applications of CB for high-voltage cables, surface heaters, communication cables, magnetic tapes, video discs, electromagnetic wave shielding materials, electrostatic inhibiting materials, electrically conductive coating materials, xerographic toners, and other organic electrically conductive materials have been developed.

In the development of these new CB materials, it goes without saying that it is an important task to render characteristics by the optimal control and design of physical and chemical properties of CB with polymers, monomers, or other compounds to be blended.

It is preferable that CB for use in the applications mentioned previously is CB with a high electrical conductivity. For example, acetylene black, conductive furnace black, channel black, the by-product carbon black from partial oxidation gas process and so on can be exemplified.

Acetylene black is obtained from high-purity acetylene gas by the thermal process or the furnace process. Conductive furnace black is [carbon] black with a high specific surface area and a high oil absorption amount (DBP) obtained by the furnace process. In particular, primary particle diameters are relatively small and porous or eggshell type particles are contained to a large extent. In the case of the development of a structure with the fusion of tens to hundreds of these particles, a high electrical conductivity is discovered even in a resin. Channel black is CB obtained by the channel process. The by-product CB is CB obtained as an oily raw material during the generation of water gas or the like by partial combustion.

These CBs contain small amounts of hydrogen and oxygen. They are present as functional groups on the surface of CB or near the surface. For example, phenol ($>\text{OH}$, weakly acidic), quinone ($>=\text{O}$), carboxylic acid ($>\text{COOH}$, strongly acidic), lactone ($>\text{COO}-$), active hydrogen ($>\text{H}$) and so on are available. These generally trap electrons and function in a direction to decrease the electrical conductivity. They are considered to render an effect on affinity during mixing with a resin or molding.

During kneading of a resin, especially PVC, with CB of a high structure, self-heat generation occurs and the pyrolysis of PVC is promoted, leading to deterioration in the quality of molded products.

In order to adjust the quality, depending on the type of CB, a trace amount of a metal salt and so on is added, or these enter during the manufacturing process. These often render an undesirable effect on the materials. The removal of this metal can be achieved by acid treatment. However, this causes a reduction in the pH of the CB. For example, in the case of kneading with PVC, the stability of PVC is decreased.

As a result of investigations on the method for the manufacture of CB having excellent properties as an electrically conductive material, it has been discovered that CB excellent as an electrically conductive material can be obtained if the CB is subjected to a heating treatment at a temperature of 250-800°C, preferably 350-400°C, for 1-10 h under an inert gas atmosphere in the presence of a higher fatty acid.

As the CB for use as a raw material, any material can be used. For example, the CBs described previously can be used. In particular, CB with a high electrical conductivity having a large surface area, preferably greater than 800 m²/g, and a DBP oil absorption amount greater than 250 mL/100 g can be used preferably.

In the case in which the CB contains a large amount of a metal, prior to the heating treatment, the CB is treated with a mineral acid, such as hydrochloric acid, sulfuric acid or the like, to carry out the metal removal. This treatment is generally conducted at a concentration of 1-10% for 1-10 h and, if necessary, at a temperature under 200°C. After the treatment, water washing is conducted. If necessary, it may be neutralized with an aqueous ammonia solution or the like, and then washed with water.

As the higher fatty acids, fatty acids with 10-20 carbon atoms, such as lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, hydroxystearic acid and other saturated fatty acids, oleic acid, linolic acid and other unsaturated fatty acids can be used. These are used at 1-10% of the CB. Prior to the heating treatment, the CB and the fatty acid are generally mixed well and then subjected to the heating treatment. If necessary, it can be used during mixing with a solvent. As a treating apparatus, for example, a rotary kiln can be used.

After the heating treatment, the desired material can be obtained by natural cooling.

By the method of the present invention, the modified CB having excellent properties can be obtained. Its action mechanism is unclear. However, it is presumed that functional groups as described previously are present on the CB surface. By the treatment of the present invention, they are partly decarboxylated and decomposed, and partly esterified to improve the pH. The active sites on the surface of the CB are decreased and affinity with respect to the resin is

increased. In particular, it is presumed that, by mixing with the resin and molding, a good effect is rendered on the surface activity of the electrically conductive material obtained.

In the case of the mineral acid treatment prior to the heating treatment of the CB, the CB is acidic. If this is mixed with PVC and molded, the PVC will be easily decomposed. For such CB, the pH is also increased by the heating treatment of the present invention. The miscibility with the resin is improved.

As will be shown in application examples to be described later, by the treatment according to the method of the present invention, the volume resistivity value is virtually unchanged. It can be understood that the reduction in the thermal stability can also be recovered and further increased by the acid treatment.

The embodiments of the present invention will be explained with application examples.

Application Example 1

60 kg of 5% hydrochloric acid were introduced into a 100-L glass flask, and 3 kg of the carbon black shown in Table 1 was also introduced and gently stirred at 95°C for 6 h. After cooling, it was filtered. Water washing was repeated until the chloride ion concentration in the filtrate was less than 10 ppm. The pH was brought to 10 by the addition of a 5% ammonia aqueous solution. The filtration and the water washing were repeated until the chloride ion concentration was less than 1 ppm. The filtration sludge was dried under vacuum to obtain demetallized treated carbon black. Its physical properties are shown in Table 1.

Table 1

	原料CB ^①	処理CB ^②
③ DBP吸油性 ml/100g	305	295
比表面積 m ² /g ④	980	996
pH	9.4	6.0
灰分 ⑤	1.1	0.03
体積固有抵抗 Ω·cm ^① ⑥	12.5	13.9
⑦ 熱安定性 分/100°C ^②	9	3

^① The value obtained by kneading 100 parts of PVC, 15 parts of CB, and 1.5 parts of lead stearate and pressing this into a sheet with a thickness of 1 mm at 180°C.

^② This represents the time until a Congo red test paper hung in the upper portion of a test tube on an oil bath changed color after short small pieces of the sheet obtained in ^① were introduced into the test tube.

- Key: 1 Raw material CB
 2 Treated CB
 3 DBP oil absorption amount mL/100 g
 4 Specific surface area m^2/g
 5 Ash content
 6 Volume resistivity $\Omega \text{ cm}^{(1)}$
 7 Thermal stability $\text{min}/190^\circ\text{C}^{(2)}$

Application Example 2

10% stearic acid was added to the hydrochloric acid treated black of Application Example 1 and mixed. This was introduced into a rotary kiln (2 in diameter x 60 cm length). While N_2 gas at atmospheric pressure was being passed through gently, the heating treatment at the temperature shown in Table 2 was conducted for 3 h. The results are shown in Table 2.

Table 2

	DBP	pH	A ($\Omega \text{ cm}$)	B (分) ①
② 処理CB (未加熱)	295	6.0	1.4	5
③ ステアリン酸添加				
④ 未加熱	263	5.4	15.5	30
200	280	5.4	15.0	34
300	280	7.1	14.8	55
350	282	7.3	14.1	60
400	285	8.8	16.7	63
600	300	9.6	17.0	68

A: Volume resistivity, B: Thermal stability [illegible; possibly, 190°C]

- Key: 1 (min)
 2 Treated CB (not heated)
 3 Stearic acid added
 4 Not heated

Application Example 3

The same implementation was conducted as in Application Example 2 except that the amount of stearic acid shown in Table 3 was used on the hydrochloric acid-treated carbon black obtained in Application Example 1. The results are shown in Table 3.

Table 3

①

ステアリン酸添加量	DBP	pH	A	B
0 %	291	7.4	12.8	8
1	290	7.2	13.0	8.5
5	288	7.7	14.0	13.5
10	282	7.3	14.1	12.5

A: Volume resistivity

B: Thermal stability (min, 190°C)

Key: 1 Amount of stearic acid added

Application Example 4

The same implementation was conducted as in Application Example 2 except that the higher fatty acid shown in Table 4 was added to the hydrochloric acid-treated carbon black obtained in Application Example 1. The results are shown in Table 4.

Table 4

①

高級脂肪酸 (添加量 5%)	pH	A (Ωcm)	B (分)
無添加 ③	6.6	10.7	9.5
イソステアリン酸	8.8	13.0	17.0
ヒドロキシステアリン酸	—	12.3	17.5
ミリスチン酸	8.8	13.6	14.0
オレイン酸	8.4	13.3	14.5

②

A: Volume resistivity, B: Thermal stability (190°C)

Key: 1 Higher fatty acid (amount of addition 5%)
 2 (min)
 3 No addition
 Isostearic acid
 Hydroxystearic acid
 Myristic acid
 Oleic acid